Effect of maleic anhydride grafted styrene-ethylene-butylene-styrene (MA-SEBS) on impact fracture behavior of polypropylene / wood fiber composites

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Abstract: MA-SEBS as compatibilizer and impact modifier was incorporated into Polypropylene/Wood Fiber (PP/WF) to enhance interface adhesion and impact strength of the composite. The effect of MA-SEBS content on the impact fracture behavior of PP/WF composites was studied. The impact properties of composites with 8% MA-SEBS reached the maximum value. And further increasing of MA-SEBS content to 10% did not improve the fracture toughness, but improved the stiffness of composites by DMA analysis. This was attributed to the improved PP/WF adhesion. As the MA-SEBS content is more than 8%, the molecule interaction of PP and WF was expected to much stronger than lower MA-SEBS. Scanning electron microscopy (SEM) was performed to analyze the impact fracture surface and showed a stronger affinity for the wood surfaces.

Keywords: Polypropylene; Wood fiber/polypropylene composites; Fracture behavior; Impact test

Introduction

Polypropylene (PP), a thermoplastic plastic, has a lot of advantages, such as good processing properties, low cost etc. However, PP has poor impact resistance under low temperature or high test speed conditions. In order to improve impact properties and low temperature toughness of PP, elastomer is often used in PP, elastomer modification of PP is known to cause dramatic reductions in both strength and stiffness. The addition of reinforcements into PP can increase the stiffness and strength, while it causes a reduction in impact toughness. Therefore, to compensate those drawbacks, a balance in the strength and toughness can be obtained by adding elastomer and reinforcement into PP. In this paper, wood fiber as reinforcement was used to improve stiffness, and MA-SEBS was used as compatibilizer and impact modifier.

Fracture toughness and impact resistance are the most important properties of polymers and their composites (Hristov *et al*. 2004a, Paul *et al*. 2001). Determination of fracture characteristics is of crucial importance. Thus, appropriate methods and conditions have to be chosen to yield meaningful data reflecting structure and properties of the materials (Williams 1984).

Reinforcing thermoplastic polymers with natural fibers has become very attractive because of the good mechanical properties that can be obtained at low cost (Qiu *et al*. 2005). The use of natural fiber as an alternative of the use of glass fiber in biodegradable material is mainly driven by ecological reasons. Wood fibers (WF) are biodegradable and nonabrasive during processing, unlike other reinforcing fibers. PP is recyclable, while WF is cheap and renewable, PP-WF composites are low cost materials and may contribute to solving environmental problems.

The Izod test is widely used for characterization of impact toughness. It is simple to perform, but it only provides the total energy consumed during the entire fracture process. A much better method for measuring the impact properties is the instrumented impact test (Hristov *et al*. 2004b). The purpose of this paper is to investigate the fracture behavior of PP/WF/MA-SEBS composites by instrumented impact test. The impact fracture surface of composites has been examined by scanning electron microscopy (SEM) and the failure mechanism of composites has been explained on the basis of interfacial fiber/matrix adhesion.

Materials and methods

Materials

Polypropylene, PP (ρ=0.91 g·cm^{-3}, the MLR= 8g·10min^{-1}, at 230ºC, 2.160 kg) as the matrix of the composites was supplied by DaQing Petrochemical Company. WF was supplied by Harbin Yongxu Co. Ltd. MA-SEBS was prepared by our laboratory with grafting ratio of 1.8%, as compatibilizer and coupler for WF/PP composites.

Preparation of composites

Wood fiber was dried at 105ºC for 24 h to remove moisture and then stored in a sealed container. In order to study the effect of MA-SEBS on the properties of WF/PP, it was decided to employ a fixed ratio of WF/PP and WF/PP as 40:60. WF/PP(PW),

WF/PP and 2% MA-SEBS(PWS2), WF/PP and 4% MA-SEBS (PWS4), WF/PP and 6% MA-SEBS (PWS6), WF/PP and 8% MA-SEBS (PWS8), WF/PP and 10% MA-SEBS (PWS10) were used. WF, PP and additives were mixed in a high speed mixer for 8 min, subsequently melted and extruded by the twin-screw extruder system. The processing temperature for extrusion was set at 150 ºC for melting zone, 170–180ºC for pumping zone and 175 ºC for die zone, respectively. The rotary speed of twin-screw was 100 r. p. m.

Impact test

Impact test of modified PP/WF was carried out by an instrumented notched Izod impact tester with 1J capacity at maximum pendulum height (160º). The tests are performed with standard size notched specimens equipped with 45º V-shaped notches of 2 mm depth and 0.25 mm root radius at the tip of the notch, we also investigated the specimens with 3, 4, 5 mm depth. The ligament lengths are 8, 7, 6 and 5 mm respectively. The specimen is impacted at velocities of 2.9 m/s. The measurement records Force–time (F-t) diagrams. Ten specimens of 80mm×10mm ×4mm were tested for each composite type. After the impact test, the fragments of the specimens were collected for fracture morphology analysis.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) only requires samples with small mass or small size that was performed with rectangular measuring system using a three-point bending. Rectangular specimens were cut from the pressed sheet to size (50 mm×10 mm×3mm). The specimens were measured using DMA242(Germany) to obtain the curves of storage modulus (E′) and loss factor (tanδ) at the fixed frequency of 1 Hz and temperature ranging from -20ºC to 200ºC, at a heating rate of 3℃/min under a flow of nitrogen.

Morphological study

The morphology of composites was observed using a FEI QuanTa200 scanning electron microscope (SEM) at an accelerating voltage of 15kv.The fracture surface of the sample was sputter-coated with gold-palladium alloy before examination. SEM micrograph magnifications were ×2000.

Results and discussion

Impact fracture characteristics

From Fig.1, we can see that PW exhibits low impact strength, because of its notch-sensitive. With adding of MA-SEBS, the impact toughness increases, this may be attributed to elasticity effects of MA-SEBS, as the MA-SEBS content is up to 8%, the impact strength reach maximum, therefore, the MA-SEBS are expected to form a flexible interface around the wood fiber, which gives the WF/PP better impact strength. It suggests that the impact toughness of PW can be improved by addition of MA-SEBS. When MA-SEBS reaches to 10%, the impact strength (σ_i) decrease slightly compared with the PWS8, which can be attributed to the molecular interaction of PP and WF increasing and the WF restriction to matrix yielding. It shows

similar trends at different ligament lengths.

The mechanical properties of elastomer and thermoplastic matrix depend on the morphology and interfacial adhesion between the matrix and elastomer. Good interfacial bond is required for effective toughening (Wu 1985). When MA-SEBS content reaches to 10%, MA can strengthen the interfacial bonding by a chemical reaction between PP and WF. MA-SEBS can also restrict the mobility of the Ethylene-Butylene (EB) block of SEBS. Thus, the PWS10 exhibits lower impact strength.

Fig.2 shows Force-time diagram for PP/WF/MA-SEBS composites at the same ligament length (L=8mm) containing 0 10% MA-SEBS under the impact conditions. It was found that the force-time curves at different MA-SEBS content are not similar to one another for every PWS sample, especially at the beginning step, the curves of PWS2, PWS4 and PWS6 are similar; while the PWS8 and PWS10 deformed in a similar way.
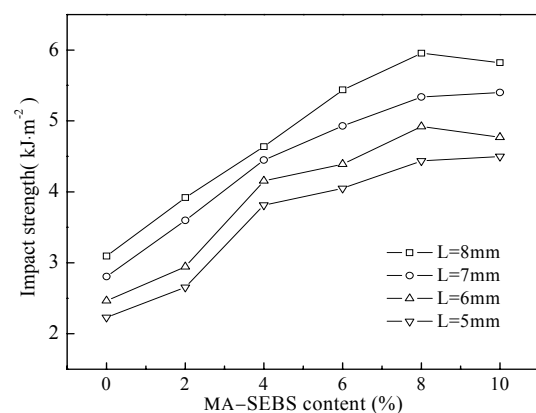

Fig.1 Impact strength (σ_i) versus MA-SEBS content (ϕ) at different ligament length

PP/WF is quite brittle when the force reaches to 35N, fracture occurs in a short time (0.6ms) at the peak of the curve and then drops off because of the fracture of brittle materials. The sample containing 2% MA-SEBS also exhibits brittle fracture, however, in this case, fracture does not occur until a much higher force. When 4% or more MA-SEBS is added to the PW composites, there is a large increase in fracture force and fracture occurs in longer time (0.9ms), which due to the more MA-SEBS providing the fracture ductility. This material shows an increased ultimate force and time relative to both PW and PWS2. The force reaches to about 55N, which indicates that 4% MA-SEBS can improve interface bonding effectly, and the total fracture energy is about 0.2 J, as a result of the higher strength and increased ductility, there is a large increase in fracture energy comparing with the samples containing 2% MA-SEBS. The decrease in force after the peak is gradual and appears descending trend, which shows improved fracture toughness.

Essential work of fracture (EWF) method

In recent years, the EWF method has been used to assess the fracture toughness of ductile polymer composites and toughened materials (Fasce *et al* 2001, Wong *et al* 1999). EWF concept was originally suggested by Broberg (Broberg 1971). This method is based on the assumption that the total fracture work for the frac-

ture of a pre-cracked specimen, the total work of fracture (W_f) is composed of the essential work required to fracture the polymer in its process zone (W_e) and the plastic work consumed by various deformation mechanisms in the plastic zone (W_p):

$$W_f = W_e + W_p \qquad (1)$$

W_e is the surface-related, whereas W_p is volume-related. W_f can be rewritten by the related specific work terms:

$$W_f = w_e tl + \beta w_p tl^2 \qquad (2)$$

$$w_f = W_f /tl = w_e + \beta w_p l \qquad (3)$$

where l is the ligament length, t the thickness of the specimen and β is a shape factor of the plastic zone. Since both w_e and w_p are material constants, and β is independent of l. Hence, it can be seen from Eq.3 that a linear relationship exists between w_f and l. By extrapolating the curve of w_f vs l to zero ligament length, w_e can be easily determined from the interception of the linear.
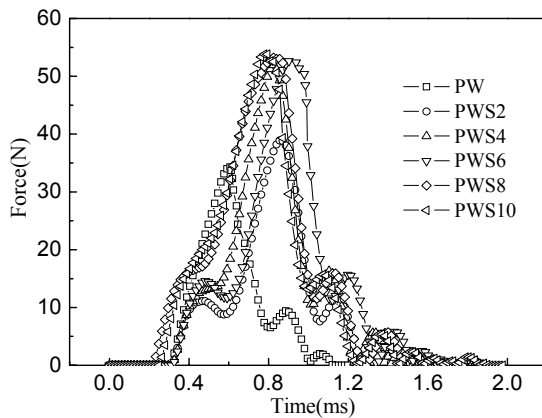

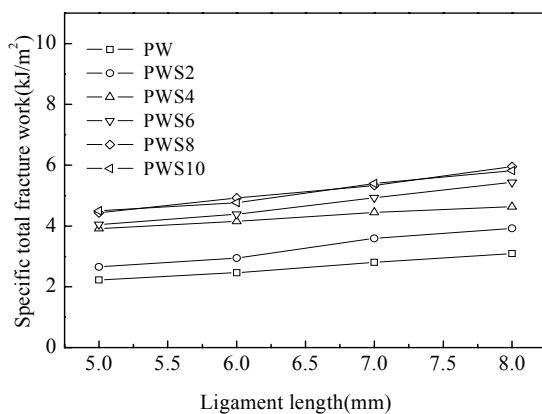**Fig. 2 Force-Time diagram for PP/WF/MA-SEBS composites with different MA-SEBS content**

Fig. 3 Plot of the specific total fracture work vs ligament for PWS with varying MA-SEBS

A plot of the specific total fracture work vs ligament length is shown in Fig.3. It can be seen that a good linear relationship

exists between specific total fracture work and ligament length, which conforms to Eq.(3). From Fig. 3, the specific essential fracture work (w_e) and βw_p can be obtained from the intercept and slope and was listed in Table 1. It can be seen that the addition of 2%–6% MA-SEBS to the PP/WF composites leads to an increase in the specific essential work of fracture or fracture toughness from 0.4741 kJ·m^{-2} to 1.6978 kJ·m^{-2}. The w_e values can be increased further to 2.1882 kJ·m^{-2} by adding 8% MA-SEBS. As the MA-SEBS content is increased to 10%, the w_e value drops to 1.9345 kJ/m^2. On the basis of EWF measurements, it appears that the MA-SEBS addition is beneficial in increasing the fracture toughness of PP/WF. The w_e increases with increasing the MA-SEBS content, which indicating that the fracture toughness of PWS can be improved by increasing MA-SEBS content. The value of βw_p is very small, which shows that most fracture energy was dissipated in the inner process zone, and plastic deformation does not take place outside the fracture process zone owing to WF restricting shear yielding of the matrix during impact tests. Accordingly, stress whitening is not observed in the plastic zone of composites.

Table 1. Specific essential fracture work for PWS with varying MA-SEBS

Samples	w_e (kJ·m^{-2})	βw_p (kJ·m^{-2})
PW	0.4741	0.2935
PWS2	0.3926	0.4441
PWS4	1.6842	0.2467
PWS6	1.6978	0.4698
PWS8	2.1882	0.4592
PWS10	1.9345	0.4965

For fiber reinforced toughened systems, Sui *et al.* (2001) pointed out that fiber-induced matrix yielding and deformation. The fracture energy mainly results from WF-matrix debonding or fiber pull-out (Tjong *et al* 2002). Synergistic toughening effects that arising from the matrix plasticity and WF pullout result in PWS8 and PWS10 hybrid exhibiting higher w_e than its matrix composites (PP/WF). This implies that the addition of MA-SEBS enhances the impact fracture toughness of the PP/WF composites.

Dynamic mechanical properties

Fig.4 (a) indicates that the storage moduli of PWS6-PWS10 are higher than that of PW and PWS (2-4) in all temperature domains, indicating an enhanced stiffness. When MA-SEBS reached to10%, the storage modulus enhance by improvement of interface bonding. The storage modulus reduced with increasing temperature, because MA-SEBS particles are already in the rubbery state, which makes storage modulus drop rapidly. In Fig.4(b), it can be seen that the peak temperatures around 0℃ (β relaxation) is due to the glass-rubber transition of amorphous portions in PP, and the temperature of β-maximum is taken as the glass-transition temperature(T_g), T_g(PP) for PWS(2-6) are changed slightly with the addition of the MA-SEBS. While T_g of PWS8 and PWS10 increase obviously, this may be attributed to improved adhesive, which is in agreement with the results of above talked about.

Fig. 4(b) also reveals that MA-SEBS additions result in an increase of the relaxation peak temperature of PP and implied the modified PP/WF composites have more restricted macromole-

cules in the amorphous phase, likely to be near WF surface. However, the MA-SEBS reaches 10%, the relaxation peak intensity of PP is lower than that of PWS8. This is due to the strong interaction that restricts the chain mobility of PP. The smaller the

loss factor tanδ, the better the interface adhesion, so the matrix toughness decrease. This is agreement with the impact data as given in Fig 1.
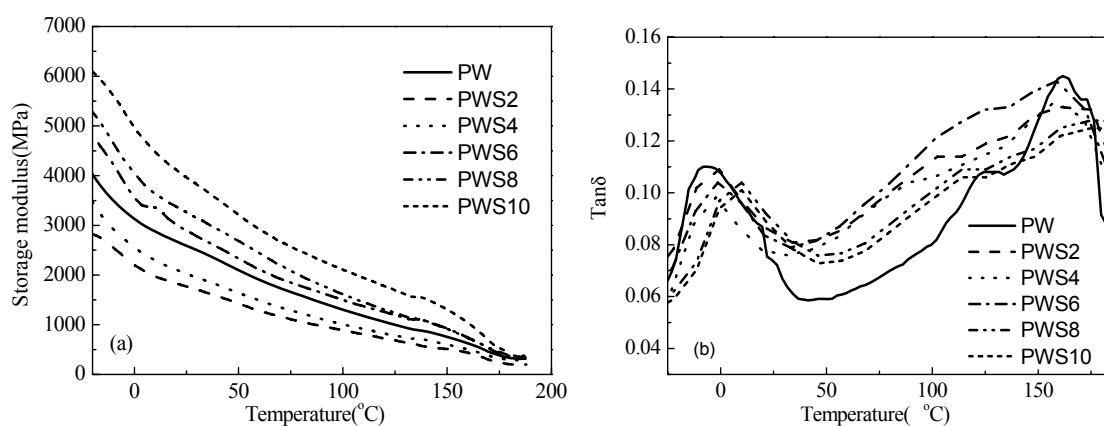

Fig. 4   Variations of (a) storage modulus and (b) tanδ with temperature for the specimens
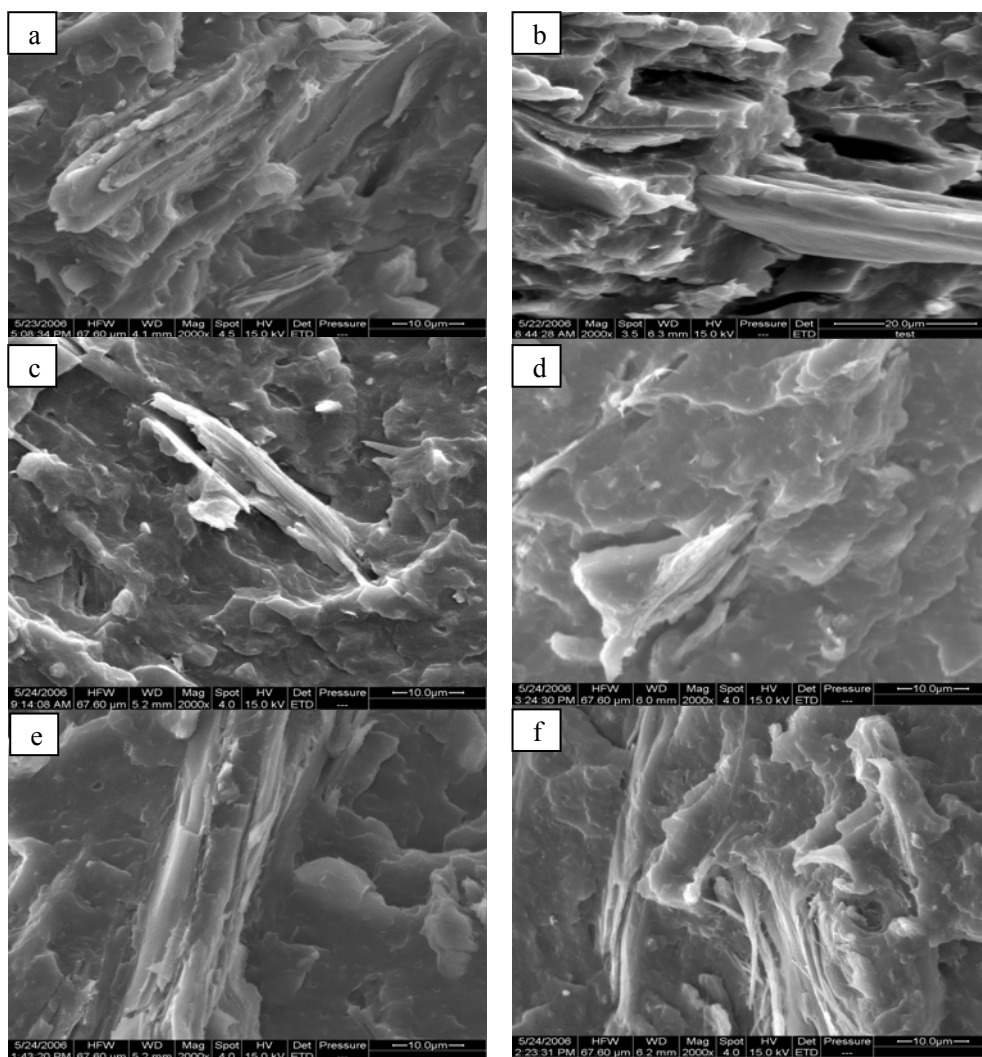

Fig. 5 SEM micrographs of samples : (a)PW; (b)PWS2; (c)PWS4; (d)PWS6; (e)PWS8; (f)PWS10

Morphology

The adhesion of PP/WF is expected to be very poor because WF has a polar group and PP has the non-polar groups. The use of compatibilizer can improve adhesion. In this study, MA-SEBS was used as a compatibilizer to improve the composite interfacial adhesion. From Fig. 5 (a), the fracture surface of the PP/WF is relatively flat, smooth and no yielding and a void is present around the wood fiber. Wood fibers are pulled out from the PP matrix, the fibers themselves show a very clean surface, which demonstrates that the interfacial adhesion between PP and WF is very weak due to weak–physical interaction based upon wood fiber break and pullout, showing the absence of plastic deformation.

The MA-SEBS (2%–6%) addition to PP/WF composites does not modify the fracture mechanism of the PP matrix. All samples present similar fracture features, because the adhesion PP/WF was not sufficient. The composites show a tendency for fiber pull-out. Moreover the WF breakage can be found in the sample. This implied that the addition of a low content of MA-SEBS to PP/WF is not sufficient to form a stress transition layer.

Some voids and deformation are found in the fracture surface of PWS (Fig. 5(e-f)), which can absorb impact energies and lead to an improvement of the toughness of PP/WF composites.

Fig. 5 (f) is the SEM photograph of impact fracture surfaces of the sample for PWS10. Apparently, the interfacial bonding between the PP and the WF is improved. It is evidence that the WF surfaces are coated with a thin layer of PP matrix. This implies that the MA group enhances the adhesion between PP matrix and WF. So, the motion of PP is limited and reduces the impact energy. It is attributed to that the MA group can react with the hydroxyl groups on the WF surface during compounding. This improves the compatibility between WF and PP matrix.

It is well known, one of the main factors that the effect the mechanical properties of fiber-reinforced material is the fiber-matrix interfacial adhesion, a weak interfacial region will reduce the efficiency of stress transfer. For the composite samples with 10% MA-SEBS content, an improvement in the adhesion of PP and WF is observed (Fig. 5-f). This observation supports the results of the impact test.

Conclusions

The study investigates the effects of MA-SEBS content on the impact properties of PP/WF composites. EWF measurements reveal that the MA-SEBS additions are beneficial in enhancing

the specific work of fracture (w_e). The PP/WF exhibits brittle fracture and nearly elastic behavior, with increasing of MA-SEBS content, which improve toughness of PP/WF composites. The impact properties of composites with up to 8% MA-SEBS reach maximum value and further increase of MA-SEBS to 10% do not improve the fracture toughness and the storage modulus is improved, this implied the improved interfacial adhesion of PP/WF.

SEM observations revealed that the deformation are responsible for the energy absorption of the composites containing MA-SEBS more than 8%, and interfacial debonding between PP matrix and WF make the toughness reach maximum value at 8% MA-SEBS. This phenomenon is due to the interfacial adhesion between PP and WF.

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